

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

**Protocol for Air Monitoring
Around a Field Application
of Chloropicrin
2005**

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (October 17, 2003 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will measure airborne concentrations of the pesticide chloropicrin around a field application. Two field-monitoring tests are scheduled to coincide with two separate applications in the Salinas area on October 3rd and October 17th 2005. The application on October 3rd will utilize the standard field tarp method, whereas the application on October 17th will utilize a new low-permeation tarp. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR.

The sampling and analysis will follow the quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version).

The sampling and analysis will follow the procedures outlined in this protocol as well as the procedures described in Attachment I, "Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (July 14, 2004 Version).

II. Sampling

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 100 standard cubic centimeters per minute (sccpm). Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are transported by vehicle to the ARB laboratory in Sacramento. DPR recommends a target 24-hour estimated quantitation limit (EQL) for chloropicrin of 0.1 ug/m³.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, needle valve, train support, and a 12 volt DC vacuum pump (see Figure 1).

Each tube is prepared in the field by breaking off each sealed glass end and immediately inserting the tube into the fitting. The tubes are oriented in the sample train with a small arrow printed on the side of each tube indicating the direction of flow. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-200 sccpm. The mass flow meter has been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates will be recorded in the field logbook (see Attachment III). The pesticide sampling procedures for adsorbent tubes are included as Attachment II. The sampling schedule consists of samples collected during daylight and overnight periods as shown below in Table 1.

Table 1
Application Sampling Schedule

<u>Sample period begins</u>	<u>Sample duration</u>
Background (pre-application)	Daytime/Overnight (two samples) 24 hours maximum
During application and post –application	Start of application until 1 hour before sunset (or until end of application if after sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

Table 2
Application Information

Location:	Scheduled for Monterey County
Field Size:	October 3 rd 12 acres; October 17 th 5.8 acres
Product Applied:	Metapicrin, 100% chloropicrin (by weight)
Type of Application:	Drip and subsequent tarp
Commodity:	Strawberries

Application Rate: Maximum label rate (100lbs/acre or higher)

Grower/Applicator: To be Determined

An attempt will be made to select a study site where there have been no chloropicrin applications to adjacent fields for at least 5 days prior to the test application and no applications anticipated to adjacent fields for three days following the test application.

A minimum of 8 samplers will be positioned, one on each side of the field and one at each corner. A ninth replicate sampler will be collocated at one downwind site. Samplers should be positioned 20 meters from the field edge. Site conditions will dictate the exact placement of samplers.

In regard to field data, the monitoring report will include: 1) a record of the positions of the monitoring equipment with respect to the field, 2) the application start location, 3) the direction of crop rows 4) how the field was divided to treat if over several days, 5) a drawing of the monitoring sites showing the precise location of the meteorological equipment, trees, buildings and other obstacles, 6) meteorological data collected at a minimum of 5-minute intervals including wind speed and direction, humidity, and air temperature and comments regarding degree of cloud cover, 7) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North), and 8) the start and end time of the application. In addition, any materials and procedures used to tarp the field will be documented.

III. Analysis

The sampling and analysis method and validation results for the sampling and analysis of chloropicrin are included as Attachment I. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour sample at 100 sccpm, the MDL and EQL would be 27.5 ng/m³ and 138 ng/m³, respectively. The DPR target EQL is 100 ng/m³. The analyses will be performed by the ARB laboratory in Sacramento.

IV. Field Quality Assurance

Field Quality Control for the application monitoring will include the following:

- 1) Four field spikes will be obtained by sampling ambient air at the application monitoring site for 24 hours (daytime/overnight). The field spikes will be obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for chloropicrin in the adsorbent tube samples will be approximately 300 ng.

- 2) Four trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.
- 3) Four lab spikes will be prepared at the same level as the field and trip spikes. The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.
- 4) Collocated (replicate) samples will be taken for all sampling periods (except the background period) at one sampling location (downwind).
- 5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

V. Sample Labeling

Samples will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where (as an example):

Location is designated as north 1, 2 or 3 (N1, N2, N3), west (W), south 1, 2 or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Chemical is designated as C for chloropicrin.

Sampling period is designated as B (for background) or 1 through 6.

The type of sample is designated as S (sample), C (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Examples:

S2-C-B-S	(South2, Chloropicrin, background, sample)
S2-C-B-FS	(South2, Chloropicrin, background, field spike)
S2-C-1-S	(South2, Chloropicrin, sampling period 1, sample)
S2-C-1-C	(South2, Chloropicrin, sampling period 1, collocated)

VI. Personnel

ARB sampling personnel will consist of staff from the MLD's Air Quality Surveillance Branch, Special Purpose Monitoring Section.

VII. Safety Recommendations

Refer to Attachment IV for general information on and toxicology of chloropicrin gas fumigant. The DPR's Monitoring Recommendations include the following safety recommendations for chloropicrin.

"The chloropicrin product labels warn that chloropicrin is a poisonous liquid and vapor and is readily identifiable by smell. Inhalation of vapors may be fatal and exposures to low concentrations of vapor will cause irritation of the eyes, nose, and throat. Exposure to high concentrations or for a prolonged period of time may cause painful irritation to the eyes or temporary blindness. Contact with the liquid will cause chemical burns to the skin or eyes and is harmful or fatal if swallowed.

The acceptable air concentration for persons exposed to chloropicrin is 0.1 ppm. If air concentrations exceed 0.1 ppm, an air purifying respirator must be worn. The highest concentrations of chloropicrin at 20 m from the field should not exceed 0.05 to 0.08 ppm. The label states that the applicator and other handlers must wear: loose fitting, long –sleeve shirt and long pants, shoes and socks, and full-face shield or safety glasses with brow and temple shields. Monitoring personnel should refer to the label of the product used and should use proper protective equipment to prevent exposure to the dust, vapors, or spray mist."

Attachment I

Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air
using Gas Chromatography/Mass Selective Detector

Attachment II

Application Sampling Procedures For Adsorbent Tubes

Application Sampling Procedures For Adsorbent Tubes

Overview:

- Collect samples, according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, from each corner sampling position.
- Collocate 1 field spike with each of the 4 background samples.
- Collect a collocated sample from one site (the downwind site) for all sampling periods (except the background period).
- Submit 1 trip blank.
- All samples are stored either in an ice-chest on dry ice or in a freezer.
- The field log sheet is filled out as the sampling is conducted. All QA samples (field and trip spikes and trip blanks) must be logged onto the log sheet.
- The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples; make and retain copies if desired.

Sampling Procedure:

Materials that will be needed to conduct the sampling include:

- Clip board with log sheets
- pencils/pens
- sample labels
- sample cartridges
- end caps
- plastic test tubes
- zip-lock bags
- 0 to 200 sccpm mass flow meter (MFM) with battery
- ice chest
- dry ice

Figure out the route for sampling the 8 locations and try to keep this the same throughout the study.

Preparation and Set-up

On the way to the study site, plug the MFM into the battery. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Securely attach one adsorbent sample cartridge to the sampling tree. **MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.**

Using the 0-200sccpm MFM set the flow rate exactly to 100 sccpm. Use the MFM calibration linear regression equation to set the flow rate.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, MFM Serial #, any comments and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment III

Field Log Sheet

Attachment IV

Chloropicrin "Information Profile"